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6. AUTHOR(S)
Roger C. Newman, Stuart B. Lyon

7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES)
University of Manchester Institute of Science and
    Technology
Corrosion and Protection Centre, P.O. Box 88,
Manchester, M60 1QD, UK

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Scientific Officer
Materials Division Code: 1131M
Office of Naval Research, Arlington, VA 22217-5000, USA
Attn: A.J. Sedriks

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This project was concerned with the link between transport and fracture in composite materials with emphasis on degradation of properties on aqueous exposure. The dependence of transport and fracture on volume fraction of a particulate filler was considered in terms of the percolation properties of the connected and unconnected particles. This report describes: validation of the percolation approach; mechanical properties and effect of water absorption; electrical and gravimetric measurements; and ternary composites with glass and rubber.

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*Environmental Interactions and Fracture
in Polymer-Matrix Composites*

Investigators: R.C. Newman and S.B. Lyon

**University of Manchester Institute of Science and Technology
Corrosion and Protection Centre
PO Box 88, Manchester, M60 1QD, UK**

AIMS AND OBJECTIVES OF THE RESEARCH

This project was concerned with the link between transport and fracture in composite materials, with particular emphasis on aqueous exposure. The dependence of transport and fracture on volume fraction of a particulate filler can be described in two dimensions by percolation theory. If there is a connected weak interface, then in two dimensions it is easy to see how the material falls apart. In three dimensions the transport problem remains tractable but fracture becomes very complex. Essentially, only a one-dimensional connection is required to facilitate transport along a randomly dispersed phase or its interfaces, but two or more dimensions are needed to describe the path of fracture through a ramified system of connected interfaces. Nevertheless, it was predicted that percolation-like phenomena would be observed in the mechanical properties of particulate composites, as well as in transport properties such as electrical resistance and water diffusion. Observation of such phenomena would provide a valuable enrichment of current models that are based on mean-field analyses and predict smooth dependences of mechanical properties on volume fraction. Experiments were conducted with glass/epoxy composites exposed to water and aqueous solutions, to test the validity of such ideas. Later ternary composites were prepared with a rubber phase as well as glass, to explore the possibility of interactive three-phase percolation phenomena that could benefit mechanical behaviour.

PRINCIPAL RESULTS OF THE RESEARCH

A very large number of tests were carried out on glass bead/epoxy composites in the range zero to 25 vol% soda (A) and borosilicate (E) glass, including:

> Electrical conductivity in dry and wet states
> Mass gain with water absorption and desorption
> Early stages of water permeation
> Elastic modulus in tension and compression, in dry and wet states
> Fracture stress in tension and "yield" stress in compression, in dry and wet states
> Fractography

Fracture toughness measurements were also carried out, but were relatively uninformative. In addition, ternary composites of glass, epoxy and rubber were tested mechanically in dry and wet states.

1.   Validation of a percolation approach for glass bead/epoxy composites

Silver-coated glass beads were used in a series of electrical conductivity measurements to validate the percolation model for this system. Whilst the resistivities were high, indicating a film of polymer between the particles, there was a transition at the right place (volume fraction of glass, q $\approx$ 0.157), indicating that the system approximates to a random biphase continuum (Figure 1).

2.   Mechanical properties of glass/epoxy composites and the effect of water absorption

In the dry state, smooth tensile specimens of glass sphere/epoxy composites showed a smooth dependence of tensile strength (equivalent to fracture stress for all but the pure polymer) on volume fraction of glass (q) - Figure 2. The strength fell up to q = 0.15, then became constant from 0.15 to 0.25. This is already a detail not observed previously, and may be interpreted qualitatively in terms of constant effective crack nucleus size above the percolation threshold (q = 0.157).

When exposed to water at moderate activity such as saturated NaCl, the polymer/glass interfaces are ruptured by glass dissolution in the case of soda glass (borosilicate glass shows less damage), but without gross osmotic damage such as occurs in de-ionized water or seawater. This proved to be a very controllable way of examining the effect of interface weakening in these composites. In particular, for q > 0.12 the strength was very low - Figure 2. It was proved electrically that this transition did occur below the percolation threshold, so it relates not to the appearance of a spanning interface cluster across the sample, but from the increase in the size of the dense part of the finite interface clusters below the threshold. Somehow this transition in interface availability causes a change in the proliferation of matrix cracks - Figure 3. The drop in fracture strength between q = 0.12 and q = 0.15 in Figure 2 (wet data) was demonstrated to be real at a high confidence level, and the transitional behaviour was especially obvious when the wet strengths were normalized to the dry strengths - Figure 4.

The degradation in tensile strength was remarkably reversible (by drying) for immersion in saturated NaCl, provided the percolation threshold was not significantly exceeded. For deionized water immersion, there was irreversible damage and loss of strength.

The behaviour of the tensile elastic modulus was less easy to interpret quantitatively than the fracture strength. New detail was apparent in the curve of modulus versus q for dry composites (Figure 5), but is not understood yet. However it is significant that particle cluster interactions must be taken into account to explain this detail. The wet materials behaved like porous polymers (Figure 5), with a decreasing modulus as glass was added. Interestingly, there was little decrease in the range 0-6% glass; this was correlated with the lack of multiple-particle clusters in this range. Osmotic pressure more easily opens up a cavity at a multiple-particle cluster than at a single spherical particle. The compressive modulus and yield stress have been measured in recent work but do not show any new features. Finally, the effect of water absorption, observed by SEM fractography, was hard to determine at high volume fractions of glass but appeared elegantly at around 6% glass - Figure 6.

Very little impairment of mechanical properties occurred at low water activities such as saturated magnesium chloride. However composites with borosilicate glass exposed to deionized water did show degradation. In most cases this was traced to sodium segregation at the surface of the borosilicate glass beads. If the beads were pre-washed to remove sodium, composites with better resistance to water could be made. No effect of sulphide additions on the sensitivty of the composites to water absorption was detected, either at pH 8 (predominantly sulphide ions) or at pH 6 (predominantly hydrogen sulphide).

3.   Electrical and gravimetric measurements on glass bead/epoxy composites during water immersion

The behaviour of these composites during water immersion contained both trivial and subtle effects. The relatively trivial case is that of osmotic interface rupture leading to a spanning water channel above but not below the percolation threshold. Figure 7 shows how this affects the eventual water uptake - at the intermediate water activity (saturated NaCl) the water absorbed is

constant up to the percolation threshold, then increases. At low water activity the interfaces do not rupture. At high water activity (deionized water) there is so much osmotic damage that large cavities are opened up even below the percolation threshold.

Electrical resistance measurements mirrored the above behaviour, but with much additional information (Figure 8). Formation of a spanning water channel was signalled by an abrupt drop in resistance. Prior to such an event, the arrival of at least two different water diffusion fronts (short-circuit and bulk transport) was observed at the midplane of the membrane - Figure 9. There was no dependence on solution conductivity indicating that there were no channels that could accommodate an electrolyte solution. Permeation measurements (Figure 10) showed that some water was permeating extremely rapidly, even in the pure epoxy, but not through pores. It was proposed that a cellular strain-induced variation in cross-link density was created during curing and provided channels for enhanced water transport.

4.   Ternary composites

Rubber was introduced into the composites in the form of carboxyl-terminated butadiene-acrylonitrile copolymer, supplied as liquid rubber by Aldrich. On copolymerizing with epoxy resin, the rubber separated as nearly spherical particles of median diameter about 5 microns. An ultramicrotome was used to prepare sections of these composites for examination (Figure 11).

In general the effect of the rubber on tensile properties of smooth specimens was detrimental, though toughness could be improved appreciably. The modulus decreased in accordance with literature models (Figure 12). The strength also decreased, with some detail similar to that seen in wet epoxy/glass composites (Figure 13). This behaviour resembled that of a porous polymer. In ternary composites, interesting improvements in properties were not seen until large volume fractions of rubber were added, e.g. 21% (Figure 14).

Fracture toughness measurements on ternary composites were not completed within the period of the grant but are underway in the remainder of Ms. Zhang's PhD period.

CONCLUSIONS AND COMMENTS ON FUTURE PRIORITIES

The main objective of this project was to test our conviction that there was hidden detail in literature curves showing mechanical properties of particulate composites versus volume fraction of filler. This objective has been realized in several interesting ways.

It was recognised that whilst a 3-D system does not fall apart at the percolation threshold in the way a 2-D one does, there is a strong change in the connectivity of the system around the threshold that must be relevant to real materials. For the brittle yet relatively tough glass/epoxy composites examined in this work, a fracture transition exists just below the percolation threshold, where the effective defect size increases sharply with volume fraction of glass particles. It would be valuable to examine the nature of this transition with controlled variations in matrix toughness. Possibly this could be done to some extent by varying the temperature. There is also a non-smooth variation of modulus with glass volume fraction, a result not previously recognised.

We have also identified simple yet new ways of using electrical resistance and permeation to monitor water effects in polymers and composites. Various intriguing short-circuit transport behaviours have been observed.

The results on ternary composites were not spectacular, possibly because the rubber used was not ideal to give a toughening action. Further work in this area is recommended using superior rubber formulations.

An interesting application of particulate composites where percolation concepts should be useful is in creep-resistant coatings for pipelines operating under extreme deep-sea conditions.

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8 L.J. Hunter, MSc thesis, University of Manchester (1993)

9 N. Islam, PhD thesis, University of Manchester (to be submitted)

10 G. Zhang, PhD thesis, University of Manchester (work still underway
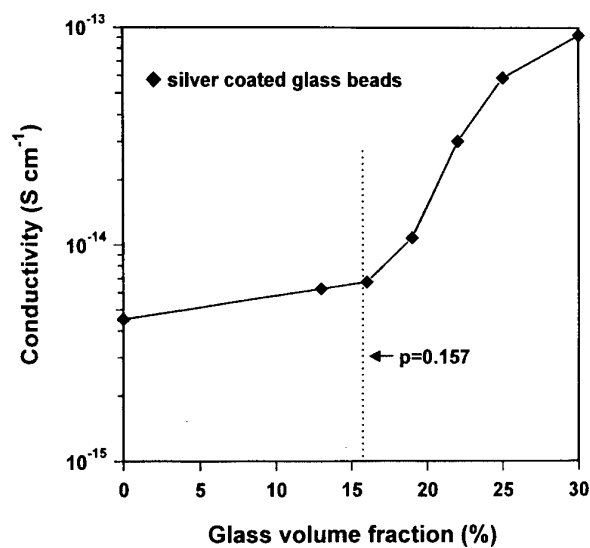
Figure 1   Demonstration that the system glass beads/epoxy resin conforms to a percolation model (conductivity measurements using silver-coated beads).
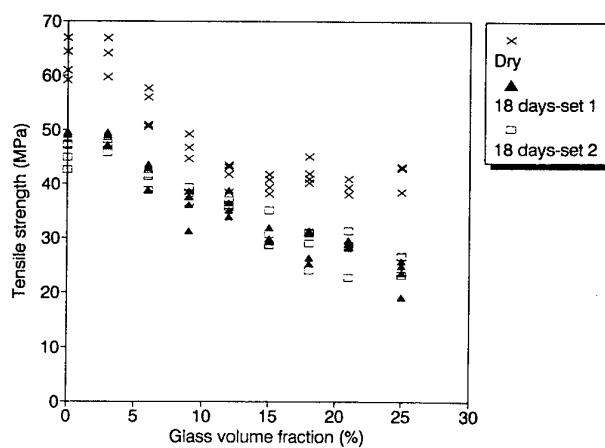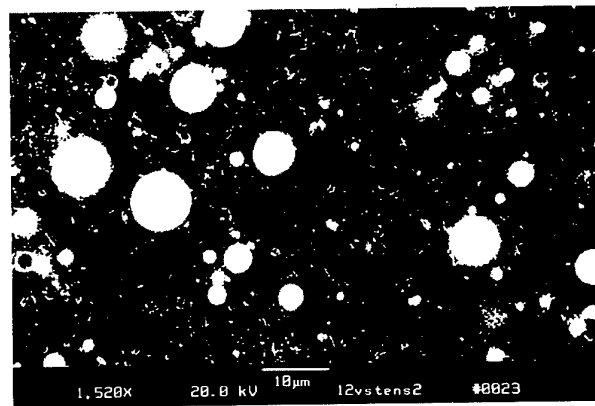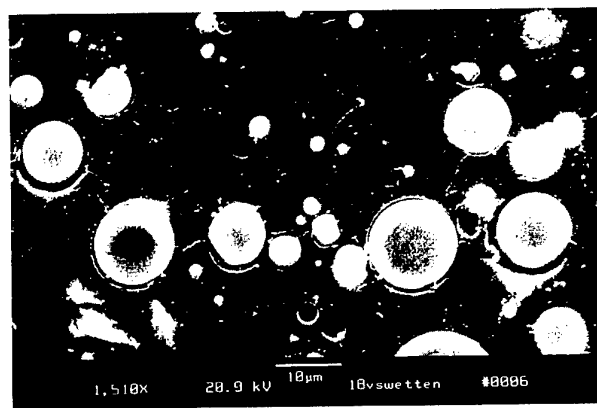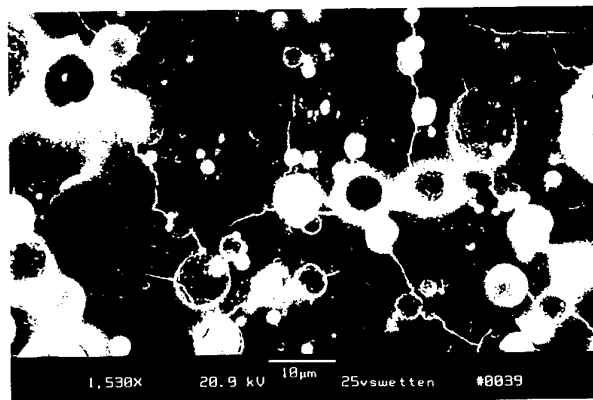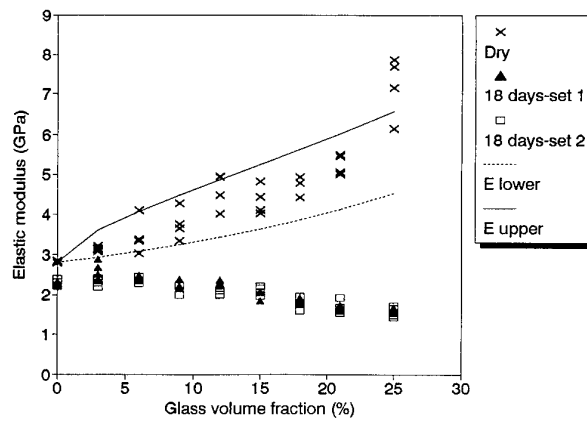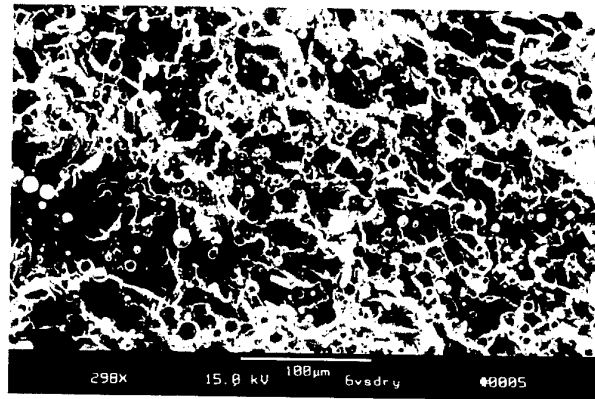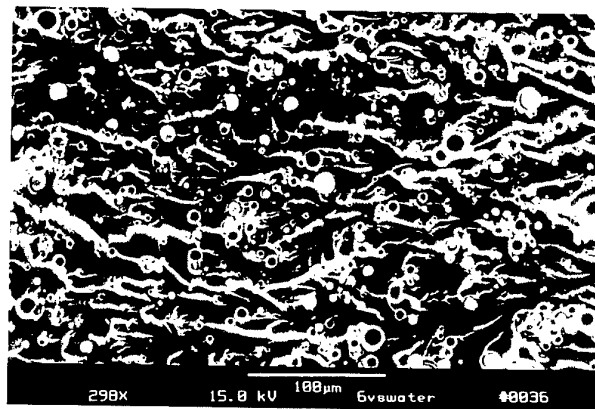

Figure 2   The effect of glass volume fraction (q) on the tensile strength of epoxy reinforced with silane-coated A-glass beads, tesed dry and after 18 days immersion in saturated NaCl solution at 40°C.

(a)

(b)

(c)

Figure 3   Polished cross-sections taken just behind the fracture surfaces of specimens of A-glass composites immersed in saturated NaCl for 18 days at 40oC, as in Fig. 2: (a) q = 0.12, (b) q = 0.18; (c) q = 0.25.
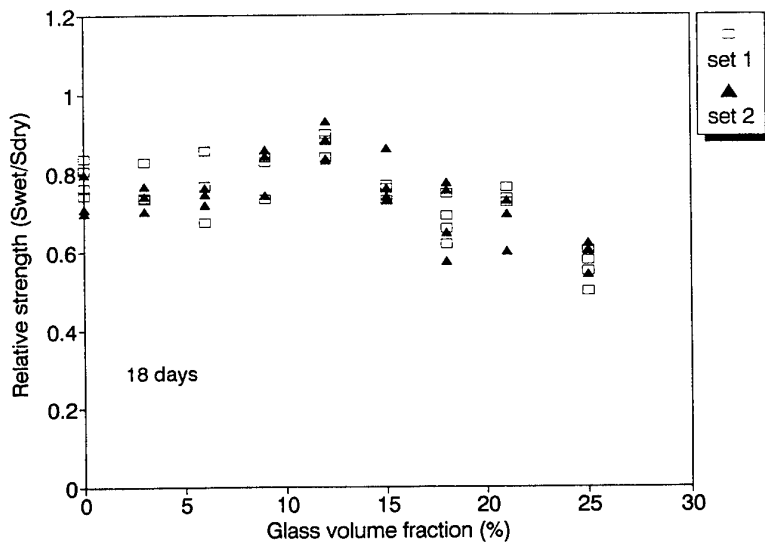
Figure 4   The ratio of wet to dry strength for the data of Figure 2.

Figure 5   The effect of glass volume fraction (q) on Young's modulus for epoxy reinforced with silane-coated A-glass beads, tested dry or after 18 days immersion in saturated NaCl solution at 40°C. The lines represent upper and lower bounds from literature models for strong interfaces.

(a)

(b)

Figure 6   Fracture surfaces of 6% A-glass composites: (a) tested dry; (b) after immersion in de-ionized water for 60 days at 40°C.
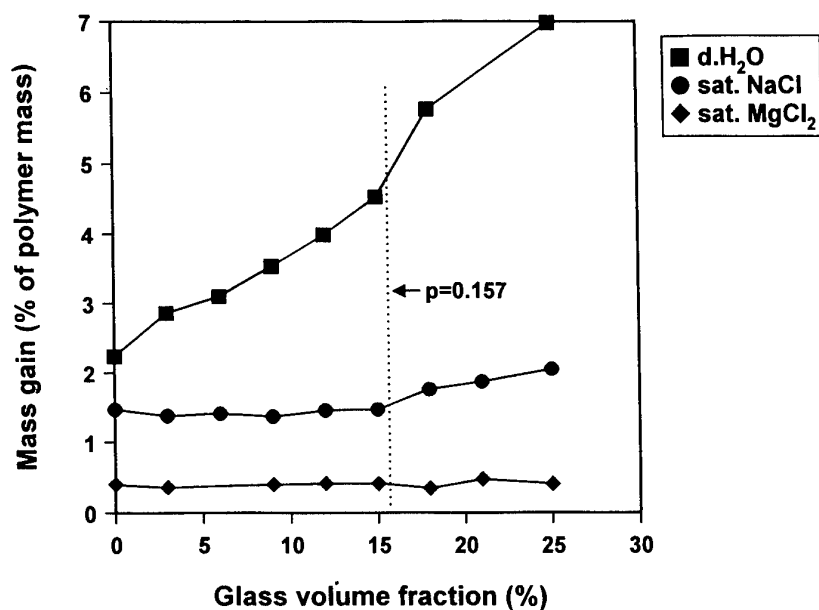
Figure 7   Effect of glass volume fraction on water uptake for epoxy reinforced with silane-coated A-glass beads after immersion for 26 days at three different water activities at 40°C.
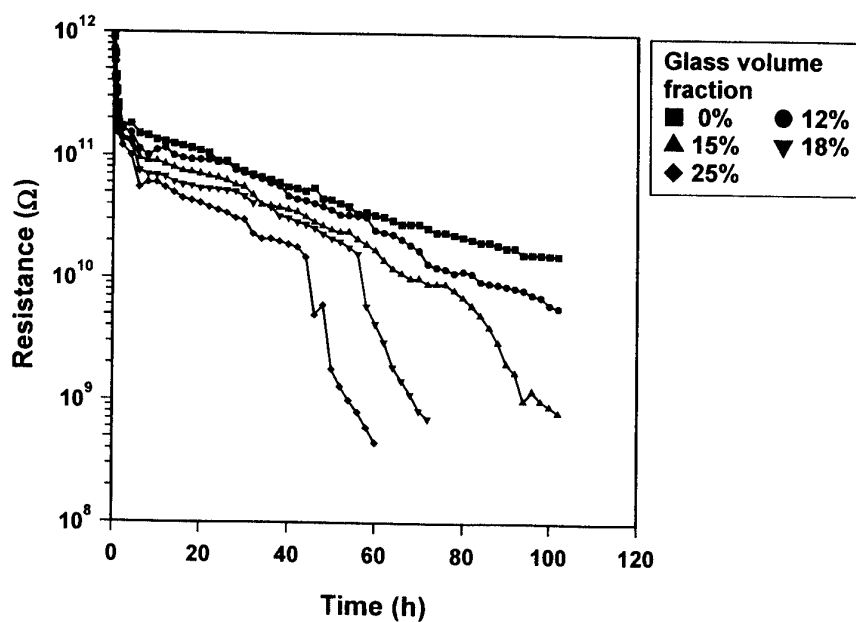
Figure 8   DC electrical resistance as a function of time during immersion in deionized water at 40°C, for 3 mm-thick discs of epoxy filled with silane-coated A-glass beads. The water had access from both sides of the membrane.
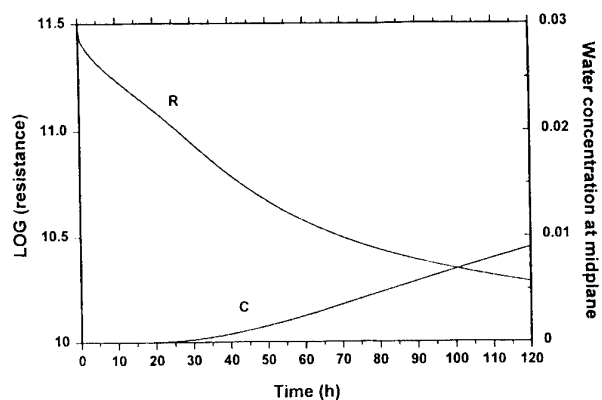
Figure 9   Example of a numerical computation of polymer membrane resistance and midplane water content for two-sided water absorption at 40°C, showing the characteristic inflection in the resistance curve - compare with Fig. 8.
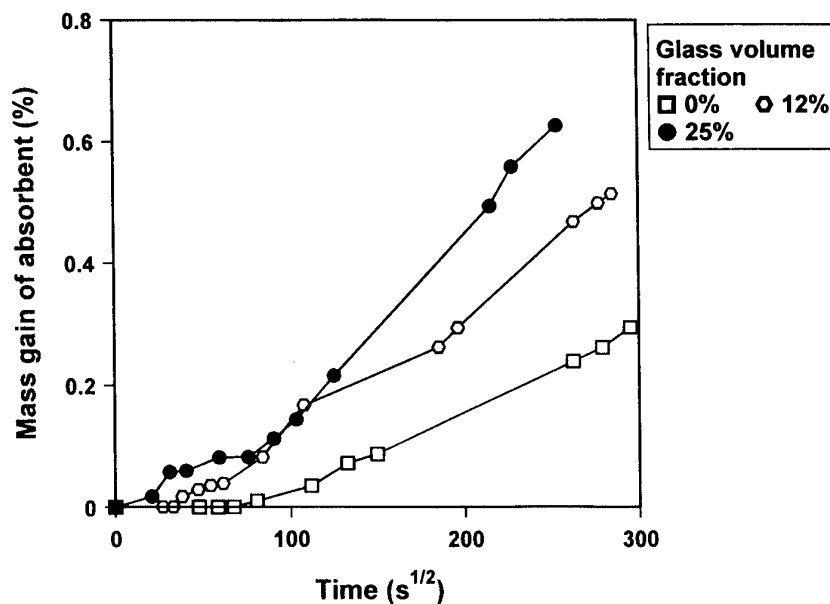

Figure 10   Water permeation through 1 mm-thick discs of epoxy reinforced with silane-coated A-glass beads, during immersion of one side in saturated NaCl at 40°C, showing short-circuit water transport.
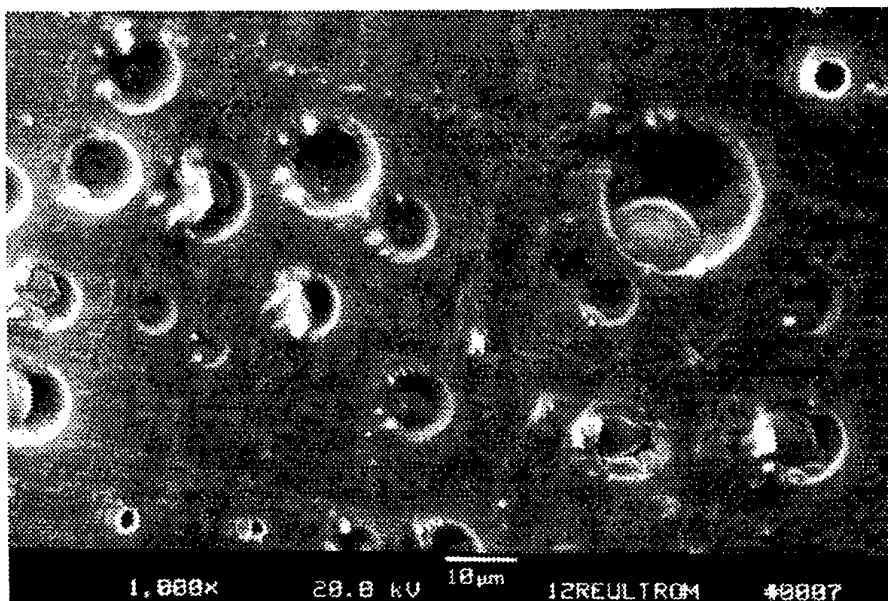
Figure 11   Ultramicrotomed surface of 12% rubber composite showing spherical cavities.
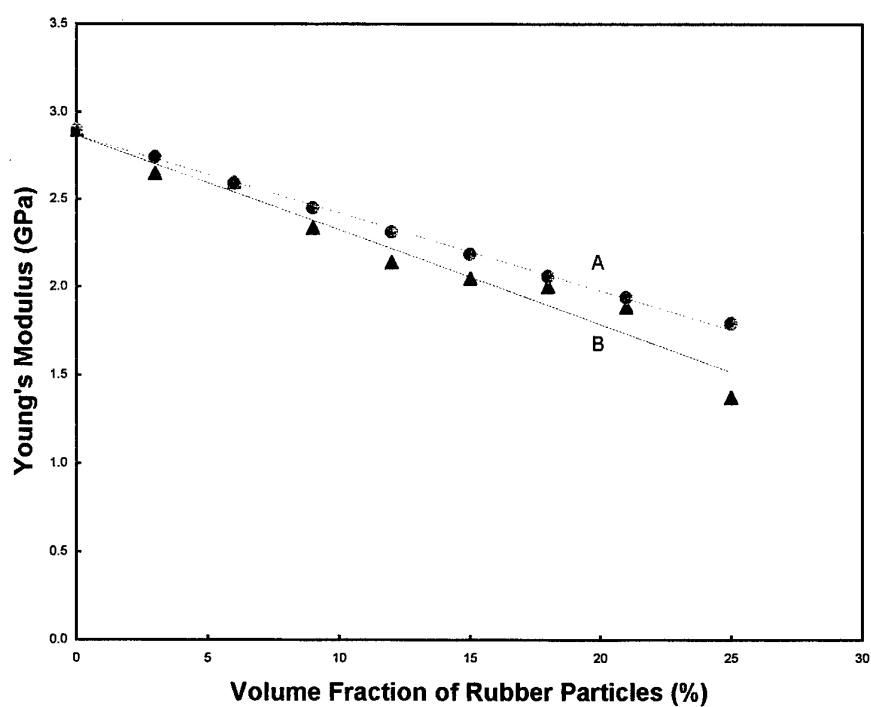

Figure 12   Young's modulus for epoxy/rubber composites as a function of volume fraction
(q) of rubber particles. Lines B is the data and Line A is from a literature model.
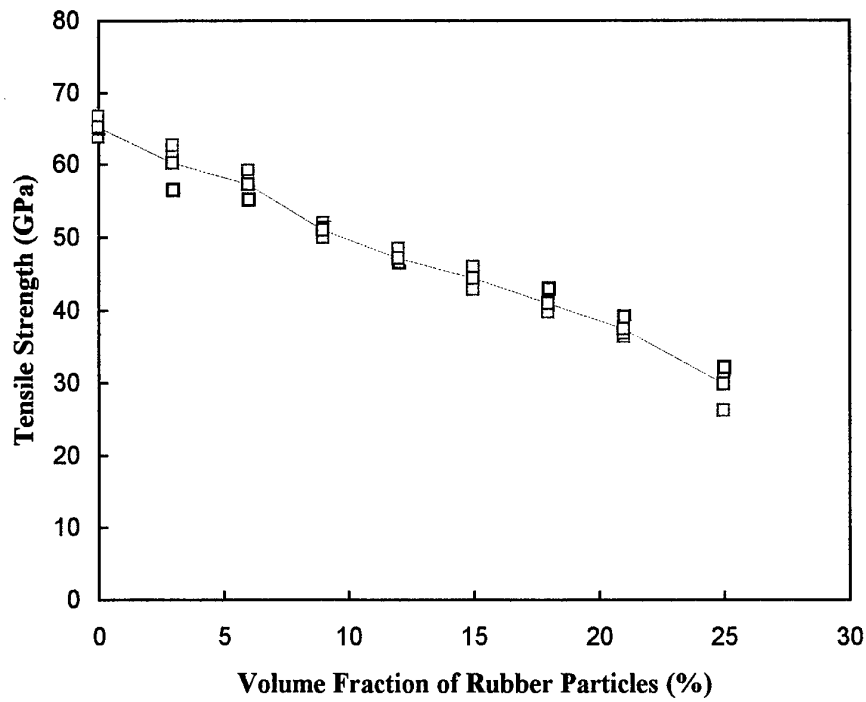
Figure 13   Tensile strength of epoxy/rubber composites as a function of volume fraction (q) of rubber particles.
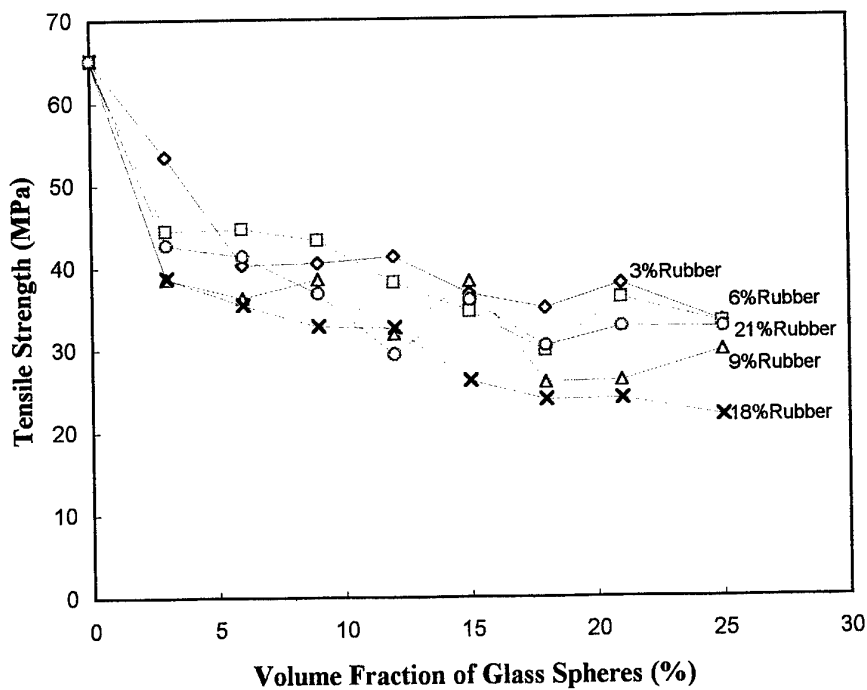

Figure 14   Tensile strength of ternary composites with various volume fractions of rubber and silane-coated glass beads, showing beginning of improvement in properties at 21% rubber.